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高锰富钴结壳还原酸浸液制备氢氧化镍钴

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摘要：富钴结壳含有钴、镍等关键金属元素，其中钴最高含量可达0.8%~1.2%。富钴结壳经还原酸浸后，镍、钴、锰元素进入浸出液，浸出液中锰浓度显著偏高，而镍钴含量相对偏低。为短流程回收镍、钴，需通过差异化沉淀实现镍、钴与锰的初步分离。鉴于氢氧化镍钴(MHP)作为制备三元前驱体所需镍钴金属的重要中间产物之一，可优先通过沉淀氢氧化镍钴的方式实现大部分镍钴与锰的分离，剩余的镍钴通过硫化沉淀镍钴的方式与锰分离。以除铁后含高锰的富钴结壳还原酸浸液为原料，采用氢氧化钠作为沉淀剂制备氢氧化镍钴。在反应温度25 ℃、氢氧化钠流速4 mL/min、氢氧化钠浓度6~8 g/L、反应时间45 min条件下，镍、钴、锰沉淀率平均分别为76.89%、60.45%、1.14%，沉淀中镍、钴合计含量平均40.57%，锰平均含量10.18%。实现了锰与大部分镍、钴的初步分离，沉淀产物可直接对接主流三元前驱体生产体系，为海洋矿产资源利用提供了新思路。

关键词：富钴结壳；还原酸浸液；高锰；氢氧化镍钴

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近些年新能源行业的快速发展[1-2]引起了动力电池行业爆发式扩张，动力电池行业对镍、钴的需求也呈现显著的增长。镍湿法冶炼的中间品有镍钴混合硫化物(MSP)和氢氧化镍钴(MHP)，可作为制备三元前驱体所需镍钴金属的重要中间产物。海底富钴结壳作为深海战略金属资源，赋存镍(0.3%~1.2%)、钴(0.2%~0.8%)、锰(15%~25%)等关键金属，可通过冶炼转化为硫酸镍、硫酸钴等电池级原料，为三元前驱体提供可持续金属供应。富钴结壳经还原酸浸后，镍、钴、锰等有价元素进入浸出液[3-5]，浸出液成分呈现高锰、低镍、低钴的特性，为实现富钴结壳还原酸浸液中镍、钴短流程回收，可优先以沉淀氢氧化镍钴的形式实现大部分镍钴与锰的分离，剩余少部分镍钴再经硫化沉淀镍钴的方式进行与锰的分离。该方法可以同时获得氢氧化镍钴和硫化沉淀镍钴硫化物两种产品，实现富钴结壳短流程制备镍钴中间产品的多样化。本文开展了沉淀氢氧化镍钴的研究。

1　试验原料与方法

1.1　原料

试验原料为除铁后的富钴结壳还原酸浸液，溶液中锰含量59.17 g/L、镍含量1.60 g/L、钴含量2.28 g/L、铜含量0.03 g/L、铁含量0.002 g/L。

1.2　方法

利用智能磁力搅拌器进行反应的搅拌和温度调控。在多口瓶内采用已标定好流量的蠕动泵分别滴加除铁后液和碱液，在恒定温度下进行沉淀反应，反应过程控制溶液pH在一定的范围内，在反应结束后

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矿浆液固分离，沉淀经洗涤、烘干后分析镍、钴、锰元素含量。通过沉淀物与原液中镍、钴、锰质量计算相应金属沉淀率。

2　结果及讨论

2.1　氢氧化钠浓度的影响

固定条件：料液流速16 mL/min、氢氧化钠浓度10 g/L、氢氧化钠流速4 mL/min、反应温度50 ℃、滴加氢氧化钠溶液时间20 min。考察氧化钠浓度对镍、钴、锰沉淀率的影响，试验结果见图1。

由图1可知，在氢氧化钠浓度由6 g/L升至10 g/L时，终点pH由7.02升高至7.06时，沉淀中的镍、钴合计含量>40%，再逐渐将氢氧化钠浓度从10 g/L提高至30 g/L，终点pH由7.11升高至7.36时，镍、钴合计含量由40.03%降至22.32%，锰含量由9.11%增加至25.93%。可见，氢氧化钠浓度低时得到的沉淀中镍、钴含量高，但是镍、钴的沉淀率低；氢氧化钠浓度高时，镍、钴的沉淀率增加，同时锰的沉淀率也增加，导致沉淀中镍、钴的含量降低。建议采用氢氧化钠浓度6~10 g/L，同时，控制pH在7.00~7.10，可以获得高品位的镍、钴沉淀物。

2.2　氢氧化钠用量的影响

固定条件：料液流速16 mL/min、氢氧化钠流速4 mL/min、反应温度50 ℃、持续滴加氢氧化钠溶液时间45 min，反应过程保持pH在7.10左右，考察氢氧化钠用量对镍、钴、锰沉淀率的影响，试验结果见图2。

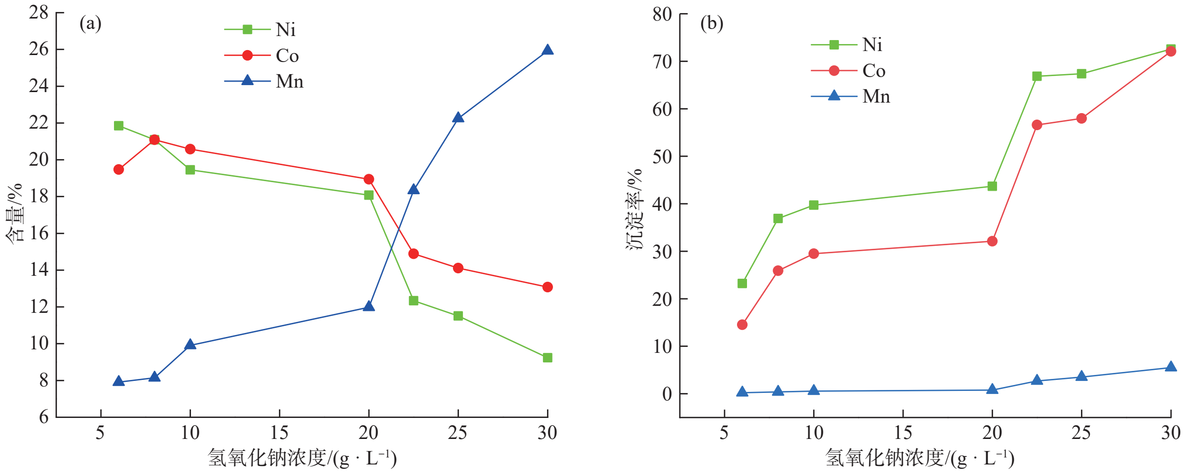

图1　氢氧化钠浓度与沉淀中镍、钴、锰含量(a)及镍、钴、锰沉淀率(b)的关系

Fig. 1　Relationships between sodium hydroxide concentration and the content of nickel, cobalt and manganese (a) and precipitation rate of nickel, cobalt and manganese (b) in the sediment

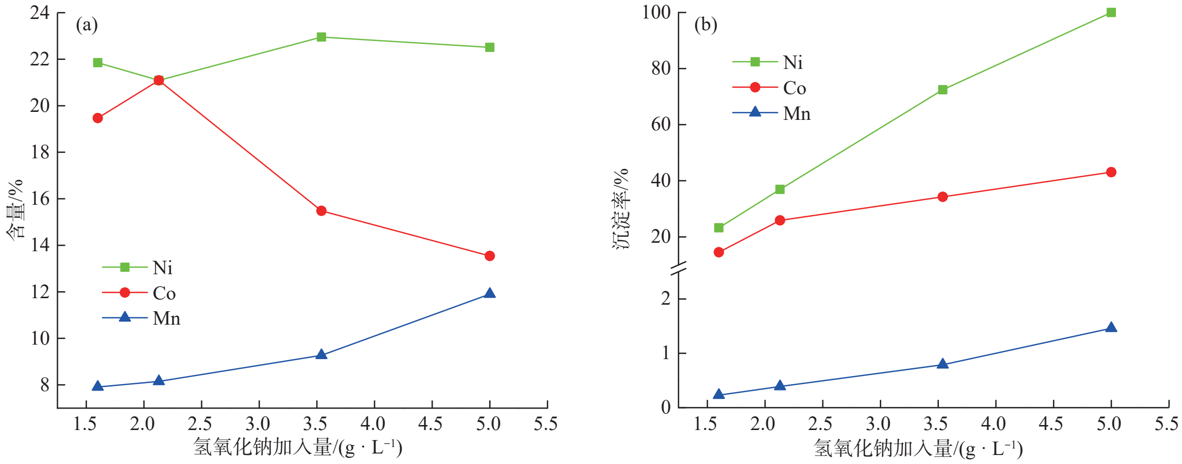

图2　氢氧化钠用量与沉淀中镍、钴、锰含量(a)及镍、钴、锰沉淀率(b)的关系

Fig. 2　Relationships between sodium hydroxide addition and the content of nickel, cobalt and manganese (a) and precipitation rates of nickel, cobalt and manganese (b) in the sediment

由图2可知,氢氧化钠用量从1.60 g/L(料液体积)增加至5.00 g/L时,沉淀中镍的含量变化不大;钴的含量呈现先增加后降低的趋势,锰的含量呈增加趋势;镍、钴、锰的沉淀率则随着氢氧化钠用量的增加而增加。可见,氢氧化钠用量增加虽然有助于提高镍、钴的沉淀率,但同时锰的沉淀率亦快速提高,影响氢氧化镍钴沉淀物的品质。需控制氢氧化钠用量在适当的范围内,以便获得高品位的氢氧化镍钴沉淀物。

2.3　流速比的影响

试验条件:氢氧化钠浓度30 g/L、反应温度50 ℃、时间20 min,考察料液流速与氢氧化钠溶液流速之比对镍、钴、锰沉淀率的影响,试验结果见图3。

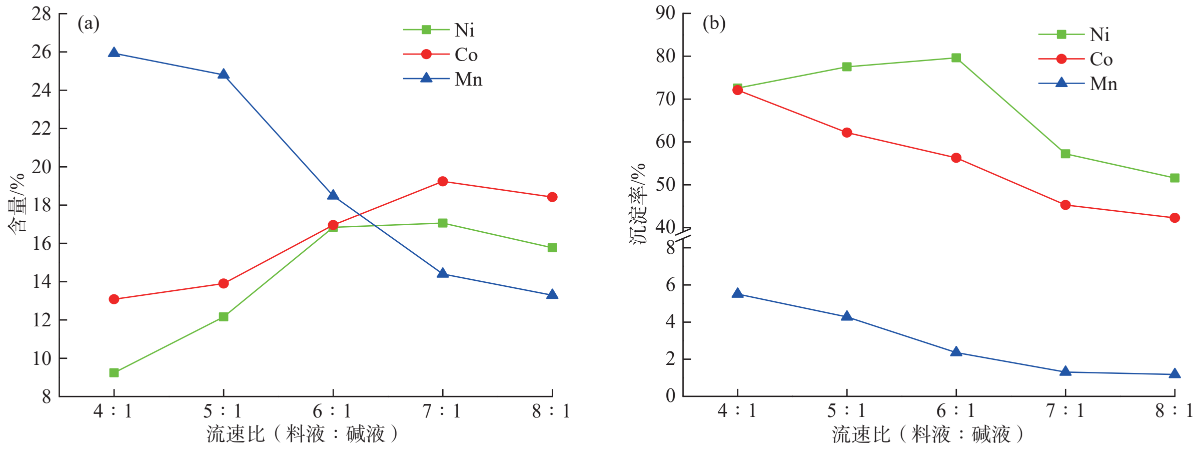

图3　料液和碱液流速比与沉淀中镍、钴、锰含量(a)及镍、钴、锰沉淀率(b)的关系

Fig. 3　Relationships between feed liquid and lye flow rate ratio and the content of nickel, cobalt and manganese (a) and precipitation rates of nickel, cobalt and manganese (b) in the sediment

由图3可知,在高浓度氢氧化钠条件下,即使增加料液与碱液的流速比,锰沉淀率依然偏高,造成沉淀中镍、钴合计含量偏低。可见,高锰溶液采用高浓度氢氧化钠溶液沉淀不利于获得高品位的氢氧化镍钴沉淀。

2.4　底液的影响

试验条件:料液流速16 mL/min、氢氧化钠浓度10 g/L、氢氧化钠流速4 mL/min、反应温度50 ℃、反应时间20 min。考察底液分别为50 mL水、50 mL料液、100 mL料液,以及碱直接滴入料液时,对镍、钴、锰沉淀率的影响,试验结果见图4。

由图4可知,随着底液由水替换成料液,沉淀中镍、钴、锰含量变化不大;料液作为底液时镍的沉淀率较水作为底液时显著增加,而钴、锰的沉淀率变化不大。可见,在氢氧化钠作为碱液时,可采用碱液直接滴入料液中沉淀镍钴氢氧化物。

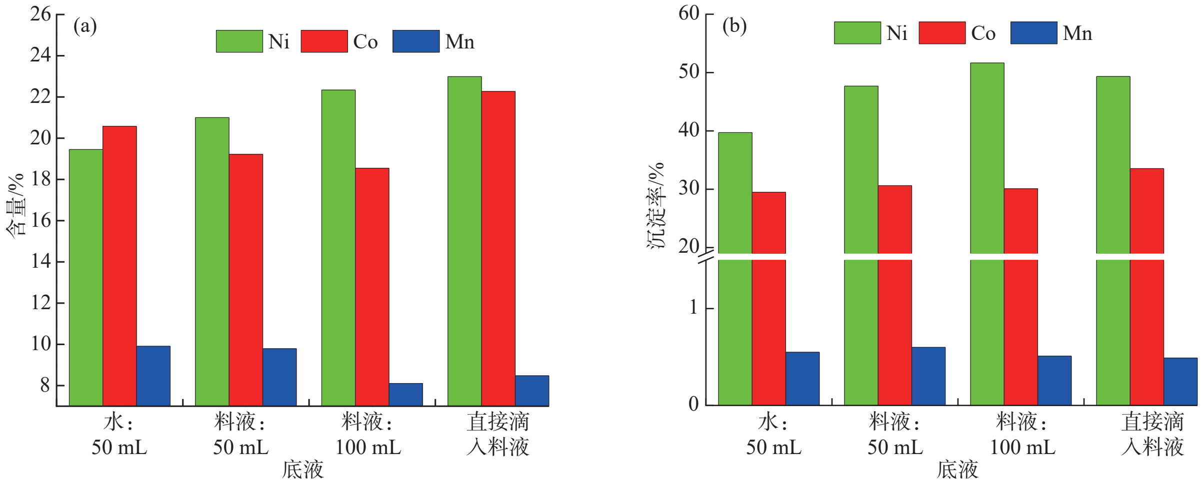

图4　底液与沉淀中镍、钴、锰含量(a)及镍、钴、锰沉淀率(b)的关系

Fig. 4　Relationships between base solution and the content of nickel, cobalt and manganese (a) and precipitation rates of nickel, cobalt and manganese (b) in the sediment

2.5 反应温度的影响

试验条件：料液流速16 mL/min、氢氧化钠浓度10 g/L、氢氧化钠流速4 mL/min、时间20 min，考察反应温度对镍、钴、锰沉淀率的影响，试验结果见图5。

由图5可知，反应温度由25 ℃升至80 ℃时，沉淀中镍的含量变化不大，钴的含量随着温度升高略微降低，锰的含量随着温度升高而增加；沉淀率方面，镍、钴、锰的沉淀率随着温度由25 ℃升至50 ℃时变化不大，当温度再提高至80 ℃时，镍、锰的沉淀率明显增加，钴的沉淀率略微降低。建议反应温度选择25 ℃。

2.6 综合条件试验

为了控制沉淀时锰的沉淀率，获得高品位的氢氧化镍钴，综合以上单因素试验结果分析，推荐综合试验条件为：温度25 ℃、氢氧化钠溶液滴入料液中、氢氧化钠流速4 mL/min、氢氧化钠浓度6%~8 g/L、时间45 min。综合条件试验结果见表1。由表1可知，在综合条件试验下，镍、钴合计平均含量40.57%，锰平均含量10.18%；镍、钴、锰平均沉淀率分别为76.89%、60.45%、1.14%。

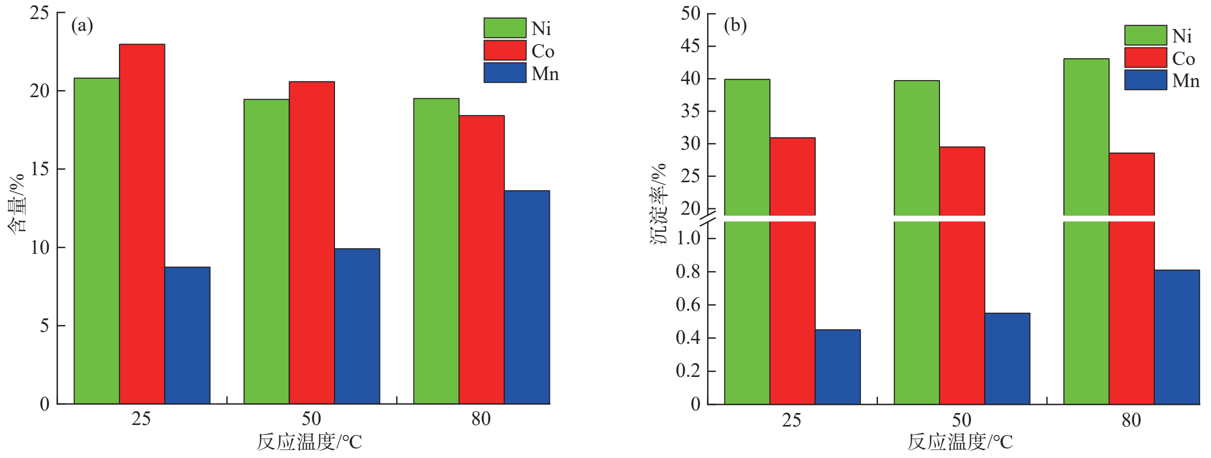

图5 反应温度与沉淀中镍、钴、锰含量(a)及镍、钴、锰沉淀率(b)的关系

Fig. 5 Relationships between reaction temperature and the content of nickel, cobalt and manganese (a) and precipitation rates of nickel, cobalt and manganese (b) in the sediment

表1 综合条件试验结果

Table 1 Comprehensive condition test results /%

编号	沉淀中元素质量分数			沉淀率		
	Ni	Co	Mn	Ni	Co	Mn
1	20.13	21.37	7.42	65.42	48.74	0.65
2	19.04	21.23	11.21	84.89	66.42	1.35
3	18.37	21.56	11.91	80.37	66.19	1.41
平均	19.18	21.39	10.18	76.89	60.45	1.14

3 结论

1）通过条件优化，在温度25 ℃，氢氧化钠流速4 mL/min，氢氧化钠浓度6~8 g/L，时间45 min时，镍、钴、锰的平均沉淀率分别为76.89%、60.45%、1.14%，沉淀中镍、钴合计平均含量40.57%，锰平均含量10.18%，实现了氢氧化镍钴产品的制备。

2）由于富钴结壳浸出液中锰含量高达约60 g/L，远远大于镍、钴的含量，沉淀氢氧化镍钴时不能完全实现镍、钴与锰的分离。结合富钴结壳还原酸浸液高锰、低镍、低钴的特点，可先沉氢氧化镍钴以实现大部分镍钴与锰的分离，剩余镍钴再硫化沉淀硫化镍钴，可实现富钴结壳短流程制备镍钴中间产品的多样化。

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Preparation of Nickel-Cobalt Hydroxide from High-Manganese Reductive Acid Leachate of Cobalt-Rich Crusts

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Abstract: Cobalt-rich crusts, also known as cobalt-rich ferromanganese crusts, are gradually becoming the focus of scientific research and industrial attention as a highly promising marine mineral resource. It is widely distributed on seamounts at water depths of 800–3 000 meters, and contains key metal elements such as nickel (0.3%–1.2%), cobalt (0.2%–0.8%) and manganese (15%–25%). These metal elements have important industrial value, especially in the battery field, which can be converted into battery-grade raw materials such as nickel sulfate and cobalt sulfate through smelting to provide a sustainable supply of metals for the ternary precursor, which is of great significance to alleviate the shortage of land resources and promote the development of new energy industry. Nickel, cobalt, and manganese are dissolved into the leaching solution after reductive acid leaching of cobalt-rich crusts. Manganese concentration in the leaching solution is significantly high, while the nickel and cobalt content are relatively low. In order to recycle nickel and cobalt in a short process, it is necessary to realize the preliminary separation of nickel, cobalt and manganese through differential precipitation. Given that nickel-cobalt hydroxide (MHP) is one of the important intermediates of nickel and cobalt metals required for the preparation of ternary precursors, separation of most of the nickel-cobalt from manganese can be achieved preferentially by precipitation of nickel-cobalt hydroxide, and the remaining nickel-cobalt is separated from manganese by precipitation of nickel-cobalt sulphide. This study utilizes high-manganese reductive acid leachate from iron-purified cobalt-rich crusts as raw material and employs sodium hydroxide as a precipitant to synthesize nickel-cobalt hydroxide. Under the optimized conditions of reaction temperature at 25 ℃, sodium hydroxide solution directly dripping into the feed solution, sodium hydroxide flow rate 4 mL/min, sodium hydroxide concentration 6–8 g/L, and reaction time 45 min, the average nickel, cobalt and manganese precipitation rate is 76.89%, 60.45% and 1.14% respectively, and the average content of nickel and cobalt combined in the precipitation is 40.57%, and the average manganese content is 10.18%. The preliminary separation of manganese from the majority of nickel and cobalt has been achieved, and the precipitated product can be directly integrated into mainstream ternary precursor production systems, offering a novel approach for the utilization of marine mineral resources. This study opens up new pathways for the comprehensive utilization of marine mineral resources. With the continuous development and refinement of technologies, cobalt-rich crusts are expected to play a more significant role in fields such as new energy and advanced materials in the future.

Key words: cobalt rich crust; reductive acid leachate; high manganese; nickel cobalt hydroxide